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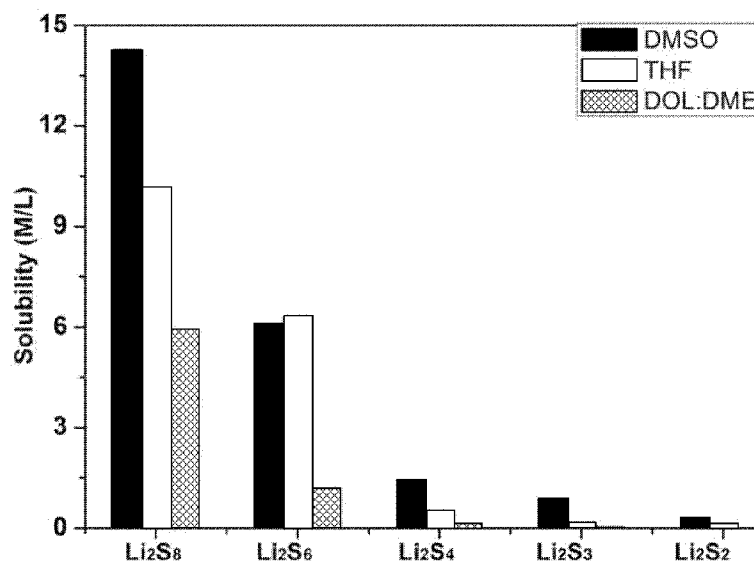
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FIG. 2



(57) Abstract: A device comprising: a lithium sulfur redox flow battery comprising an electrolyte composition comprising: (i) a dissolved Li₂S_x electroactive salt, wherein $x \geq 4$; (ii) a solvent selected from dimethyl sulfoxide, tetrahydrofuran, or a mixture thereof; and (iii) a supporting salt at a concentration of at least 2 M, as measured by moles of supporting salt divided by the volume of the solvent without considering the volume change of the electrolyte after dissolving the supporting salt.

ELECTROLYTE FOR STABLE CYCLING OF HIGH-ENERGY LITHIUM SULFUR REDOX FLOW BATTERIES

CROSS REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. Patent Application No. 14/530,442, filed October 31, 2014, which is incorporated herein by reference in its entirety.

STATEMENT AS TO RIGHTS TO INVENTIONS MADE UNDER FEDERALLY-SPONSORED RESEARCH AND DEVELOPMENT

This invention was made with government support under Contract DE-AC0576RLO1830 awarded by the U.S. Department of Energy. The government has certain rights in the invention.

BACKGROUND

High energy non-aqueous lithium sulfur (Li-S) redox flow batteries are of interest, particularly for stationary applications. However, the presence of insoluble short-chain polysulfides largely sacrifices the theoretically high energy opportunity due to deposition of $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ onto the current collectors (for example, graphite felt). In addition, the unstable interface between the conventional electrolyte and the lithium metal anode surface also limits the long-term cycling performance of the redox flow batteries.

SUMMARY

Disclosed herein is a device comprising:

a lithium sulfur redox flow battery comprising an electrolyte composition comprising:

(i) a dissolved Li_2S_x electroactive salt, wherein $x \geq 4$;

(ii) a solvent selected from dimethyl sulfoxide, tetrahydrofuran, or a mixture thereof; and

(iii) a supporting salt at a concentration of at least 2 M, as measured by moles of supporting salt divided by the volume of the solvent without considering the volume change of the electrolyte after dissolving the supporting salt.

Also disclosed herein is an energy storage system comprising:

a lithium sulfur redox flow battery comprising an electrolyte composition comprising:

(i) a dissolved Li_2S_x electroactive salt, wherein $x \geq 4$;

(ii) a solvent selected from dimethyl sulfoxide, tetrahydrofuran, or a mixture thereof; and

(iii) a supporting salt at a concentration of at least 2 M, as measured by moles of supporting salt divided by the volume of the solvent without considering the volume change of the electrolyte after dissolving the supporting salt; and

a source of the electrolyte composition fluidly coupled to the lithium sulfur redox flow battery.

The foregoing will become more apparent from the following detailed description, which proceeds with reference to the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic representing one embodiment of an energy storage system disclosed herein.

Fig. 2 is a graph depicting the solubility of Li_2S_x in pure dimethyl sulfoxide (DMSO), tetrahydrofuran (THF) and 1,3-dioxolane (DOL) and dimethoxyethane (DME) co-solvent (DOL:DME). Solubility for Li_2S_x is calculated based on elemental sulfur S.

Fig. 3 is a graph demonstrating the effect of LiTf on increasing the solubility of Li_2S_2 in DMSO solvent.

Fig. 4 is a graph demonstrating the solubility of Li_2S_x in DMSO_{30} :LiTf mixture.

Figs. 5a and 5b show the charge/discharge curves in Li-S batteries in (a) 1M and (b) concentrated (2 M) electrolyte consisting of LiTf in DMSO solvent.

Fig. 6 is a graph showing the effect of LiTFSI on increasing the solubility of Li_2S_2 in DMSO solvent.

Figs. 7a and 7b shows the charge/discharge curves of Li-S batteries using (a) 1M and (b) concentrated (3 M) electrolyte comprised of LiTFSI in DMSO. (Note: the S cathode used here was dissolved into DMSO electrolyte in the form of Li_2S_x).

Figs. 8a and 8b are graphs showing (a) the cycling performance and (b) the Coulombic efficiency of Li-S batteries in 1M and concentrated (3 M) electrolytes comprised of LiTFSI in DMSO-based electrolyte, respectively. (Note: the S cathode used here was dissolved into DMSO electrolyte in the form of Li_2S_x).

DETAILED DESCRIPTION

The following explanations of terms and abbreviations are provided to better describe the present disclosure and to guide those of ordinary skill in the art in the practice of the present disclosure. As used herein, "comprising" means "including" and the singular forms "a" or "an" or "the" include plural references unless the context clearly dictates otherwise. The term "or" refers to a single element of stated alternative elements or a combination of two or more elements, unless the context clearly indicates otherwise.

Unless explained otherwise, all technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the art to which this disclosure belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present disclosure, suitable methods and materials are described below. The materials, methods, and examples are illustrative only and not intended to be limiting. Other features of the disclosure are apparent from the following detailed description and the claims.

Unless otherwise indicated, all numbers expressing quantities of components, percentages, temperatures, times, and so forth, as used in the specification or claims are to be understood as being modified by the term "about." Accordingly, unless otherwise indicated, implicitly or explicitly, the numerical parameters set forth are approximations that may depend on the desired properties sought as known by those persons of ordinary skill in the art or limits of detection under standard test conditions/methods, as known to those persons of ordinary skill in the art. When directly and explicitly distinguishing embodiments from discussed prior art, the embodiment numbers are not approximates unless the word "about" is recited.

To facilitate review of the various embodiments of the disclosure, the following explanations of specific terms are provided:

Cell: As used herein, a cell refers to an electrochemical device used for generating a voltage or current from a chemical reaction, or the reverse in which a chemical reaction is induced by a current. Examples include voltaic cells, electrolytic cells, redox flow cells, and fuel cells, among others. A battery includes one or more cells. The terms "cell" and "battery" are used interchangeably only when referring to a battery containing a single cell.

Half-cell: As used herein, a half-cell is an electrochemical cell including a lithium metal negative electrode, another working electrode as the positive electrode, a separator, and an electrolyte.

The volume energy density of a redox flow battery can be calculated from the following equation:

$$E = n \cdot 26.8 \cdot M \cdot \text{OCV} \text{ (Wh/L)} \quad \text{Eq(1)}$$

where n is the electron transfer number, M is the concentration of catholyte; OCV is the open circuit voltage of the cell.

From Eq(1), the higher concentration the higher volumetric energy density in a redox flow battery, thus it is critical to increase the concentration of catholyte/anolyte to improve the volumetric energy density of a given system.

In the case of Li-S redox flow batteries, the higher the solubility of Li_2S_x , the higher energy density would be achieved. Furthermore, high solubility is needed not only for starting species like soluble Li_2S_8 , it is also very critical for the discharge product Li_2S_2 which is nearly insoluble. Otherwise, the insoluble Li_2S_2 easily blocks the porous current collector (graphite felt) and terminates the cell operation.

Thus, disclosed herein are energy storage systems that include a non-aqueous lithium sulfur (Li-S) redox flow battery device that includes a novel electrolyte composition that increases the solubility of short-chain polysulfides such as Li_2S_2 and enable the stable cycling of lithium metal anodes. An example of one embodiment of an energy storage system is shown in Fig. 1. The redox flow battery device includes a catholyte solution 2 that is in contact with a current collector 4. The redox flow battery also includes an

anode electrode 7. The catholyte solution 2, the current collector 4 and the anode electrode 7 may be arranged in a redox flow battery compartment 15.

The catholyte solution includes particular combinations of a solvent and a high concentration of at least one supporting salt that increase the solubility of short-chain polysulfides such as Li_2S_2 and enable the stable cycling of lithium metal anodes.

Dimethyl sulfoxide (DMSO) is a strong high polar solvent, which shows higher solubility for high order lithium polysulfide Li_2S_x ($x \geq 6$). However, for low order lithium polysulfide ($x \leq 4$), the solubility in pure DMSO is quite low (Fig. 2.). In addition, although the DMSO-based solvent has been identified to improve polysulfide solubility, the compatibility of Li anode with DMSO-based electrolyte is a concern in a Li-S redox flow battery. Usually lithium metal cannot be cycled at all in DMSO-based electrolyte due to intense side reactions between DMSO and lithium. It has now surprisingly been found that a combination of a specific solvent, DMSO and/or THF, and a high concentration of at least one supporting salt synergistically cooperate to provide both increased solubility of low order Li_2S_x electroactive salts and enable reversible cycling of a Li metal anode.

In particular, the catholyte solution includes a solvent selected from DMSO, THF, or a mixture of DMSO and THF. In certain embodiments, the catholyte solution consists essentially of, or consists of, DMSO. In certain embodiments, the catholyte solution consists essentially of, or consists of, THF. In certain embodiments, the catholyte solution consists essentially of, or consists of, a mixture of DMSO and THF.

The supporting salt in the catholyte solution may be selected from lithium trifluoromethanesulfonate ($\text{CF}_3\text{SO}_3\text{Li}$, LiTf), lithium bis(trifluoromethanesulfonyl) imide ($\text{LiN}(\text{SO}_2\text{CF}_3)_2$, LiTFSI), LiCF_2CO_2 , LiNO_3 , or a mixture thereof. In general, the concentration of at least one of the supporting salts should be at least 2M, particularly greater than 2 M, more particularly at least 3 M, and most particularly at least 4 M, as measured by moles of supporting salt divided by the volume of the solvent without considering the volume change of the electrolyte after dissolving the supporting salt. In other words, x M means x M supporting salt/1 L solvent. When the supporting salt concentration is greater than 5 M, the utility of sulfur becomes low due to increased viscosity.

The electroactive salt in the catholyte solution may be selected from any Li_2S_x salt (where $x \geq 4$). In certain embodiments, the electroactive salt is Li_2S_8 .

Listed below are illustrative embodiments of catholyte solutions (the Li_2S_8 concentration is based on elemental sulfur):

1) 0.5-4 M Li_2S_8 dissolved in DMSO solvent with 2M-4 M LiTFSI as supporting salt.

2) 0.5-4 M Li_2S_8 dissolved in DMSO solvent with 2M-4 M LiTFSI and 0-0.5 M LiNO_3 as supporting salt.

3) 0.5-6 M Li_2S_8 dissolved in DMSO solvent with 2M-4 M LiTFSI and 0.001-1 M LiTf as supporting salt.

4) 0.5-6 M Li_2S_8 dissolved in DMSO solvent with 2M-4 M LiTFSI, 0.001-1 M LiTf and 0-0.5 M LiNO_3 as supporting salt.

The anode electrode may be a lithium metal (with or without a passivation layer), graphite, tin or a tin alloy with another metal, or porous silicon.

5 The current collector may be a porous carbon electrode such as graphite felt, or where the carbon is a carbon nanofiber, a carbon nanotube, or graphene; a porous carbon electrode modified with metal and/or metal oxide, such as Pt, Au, MnO_2 , or ITO; or a porous carbon electrode modified by a functional group such as $-\text{COOH}$.

10 In certain embodiments of the system shown in Fig. 1, the redox flow battery 15 includes a first half cell part 20 and a second half cell part 21. In certain embodiments, the first cell part 20 is contiguous with the second cell part 21. The first cell part 20 includes the catholyte solution 2 and the current collector 4. The second cell part 21 includes the same catholyte solution 2 for Li_2S_x free common electrolyte that is in contact with the anode electrode 7. A separator 8 is located between the first half cell 20 and the second half cell 21.

15 In certain embodiments, there is no separator. In the separator-less embodiment there are not first and second half-part cells.

Also disclosed are energy storage systems that include a catholyte solution source 1 (e.g., a tank) in fluid communication with the redox flow battery compartment 15. A flow conduit 3 fluidly couples the source 1 to the compartment 15. For example, the first half cell part 20 may include ports connected to the flow conduit 3. A pump 5, or some other fluid motive device, is in fluid communication with the flow conduit 3. The system may also include a flow controller for electrolyte maintenance. The conduit and flow controller can be configured to permit or restrict circulation of electrolyte solution from the first half cell part 20 to the second half cell part 21, and vice versa. The first half cell part 20 and the second half cell part 21 are configured to be flow cells.

25 The system also includes an external electrical load 6 coupled to the current collector 4 and the anode 7.

In certain embodiments, the catholyte solution and the anolyte solution are substantially the same solution and/or are sourced from a common solution. In certain embodiments with an ion selective membrane separator, the anolyte may include a salt such as LiTFSI or LiFSI dissolved in an ether solvent such 1,2-dimethoxyethane (DME), or an alkyl carbonate solvent such as propylene carbonate (PC), ethylene carbonate (EC), or dimethyl carbonate (DMC).

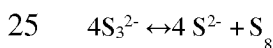
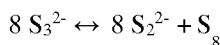
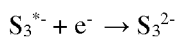
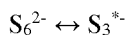
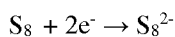
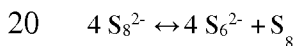
The redox flow battery compartment can be configured as a flow cell in fluid communication with a source of the catholyte solution. In certain embodiments, the first half cell 20 can be configured as a flow cell in fluid communication with catholyte source 1.

35 In certain embodiments, the separator 8 may be a porous membrane material. Examples of the membrane can include, but are not limited to, ion-exchange membranes, polymer membranes, and solid-state membranes the comprise polymer(s), sulfonated tetrafluoroethylene based fluoropolymer-

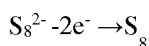
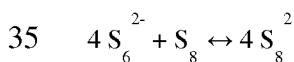
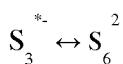
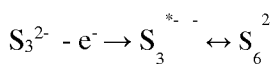
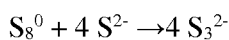
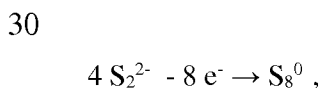
copolymer(s), and ceramics. Examples of a porous separator include, but are not limited to, nano- and micro-porous separators that comprise polymer(s), ceramic(s), glass(es) or other materials. Non-limiting examples of suitable separator materials include, NAFION- type ion exchange membranes (sulfonated tetrafluoroethylene-based fluoropolymer-copolymers), other porous polymeric materials such as, for example, sulfonated poly(ether ether ketones), polysulfones, polyethylene, polypropylene, ethylene-propylene copolymers, polyimides, polyvinylidene difluorides, and the like, which can be in the form of membranes, matrix-supported gels, sheets, films, or panels. Other suitable materials include porous ceramics, porous insulated metals, cation-conducting glasses, and zeolites. Alternatively, the separator can be an interface between immiscible liquids. In such case, a porous film, panel, or mesh might be included to aid in maintaining separation between the liquids (e.g., as a physical support or guide to aid in maintaining laminar flow at the interface).

The redox flow battery device has a prior-to-charge state in which the catholyte comprises the components described above. This means that the catholyte solution includes S_8^{2-} and optionally at least one species selected from S_8^0 , S_6^{2-} , S_4^{2-} , S_3^{*-} .

During discharging of the battery, the current collector and the anode electrode are placed in a circuit (e.g., with an external load such as a power grid), while simultaneously pumping the catholyte over the cathode current collector. S_8^{2-} and/or S_m^{2-} species are reduced to S_3^{*-} , S_2^{2-} and/or S^{2-} and stored in the catholyte. Reduced catholyte flows through the cathode current collector, and back to the tank 1. During discharging the following reactions may be occurring:

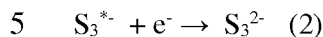
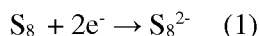


During charging of the battery, an electric potential is applied to the cathode and anode current collectors, with the stored reduced catholyte being pumped back over the cathode current collector again to be oxidized. During discharging the following reactions may be occurring:



After charging and discharging, the catholyte again comprises the components described above.

The redox active species may be:



In which, reaction (1) is dominate reaction at higher voltage; reaction (2) is the dominate reaction at a lower voltage.

Certain metal-ligand coordination also possibly may be produced during charge/discharge process, such as $(DMSO)_n(LiTFSD)_m(Li_2S_x)_l$ ($m, n, l \geq 0$).

10 Compared with aqueous redox flow cells, the volume energy density of the presently disclosed systems is much higher due to the increased voltage and capacity. For example, in certain embodiments, the non-aqueous redox flow batteries may have volume energy density values that are greater than 50 Wh/L, or greater than 100 Wh/L. In addition, sulfur is very cheap thus reducing the cost.

15 Examples

Lithium trifluoromethanesulfonate (LiTf) comprised of Tf⁻ anion with high ionic association, was used as an additive to enhance the solubility of low order Li_2S_x in DMSO solvent. Fig. 3 shows the effect of LiTf addition on increasing solubility for insoluble Li_2S_2 at different LiTf concentrations in DMSO solvent. For salt/solvent mole ratio of 30 ($DMSO_{30}:LiTf$), the solubility of Li_2S_2 can be increased almost ten times
20 higher than that in pure DMSO solvent. The solubility of other polysulfides with different chain lengths is also improved after the addition of LiTf (Fig. 4).

Concentrated salt electrolyte is employed to improve the capability of Li anode with DMSO-based electrolyte. When 1M LiTf in DMSO is used in a Li-S battery, the charge-discharge curves show large
25 fluctuations (Fig. 5a) due to the unstable interface between DMSO and lithium metal. When LiTf concentration is increased to more than 1M, the curves in Fig. 5b became smoother. It was found that if LiTf was replaced by LiTFSI, similar increased solubility of short-chain polysulfides can be reached (Fig. 6). Again, 1M LiTFSI in DMSO has abnormally long charge plateau due to the instability of Li metal in DMSO (Fig. 7a). Increasing LiTFSI concentration effectively prevents the parasitic reactions during charge (Fig.
30 7b). Significantly improved cycling stability (Fig. 8a) and Columbic efficiency (Fig. 8b) are observed in concentrated LiTFSI electrolytes with high reversible capacity at ca.1000-1200 mAh/g. These examples were performed with stationary button cells, with carbon sheet as cathode current collector, dissolved Li_2S_x in DMSO-based solvent as catholyte, and Li counter and reference electrodes.

35 In view of the many possible embodiments to which the principles of the disclosed systems, devices and compositions may be applied, it should be recognized that the illustrated embodiments are only preferred examples of the invention and should not be taken as limiting the scope of the invention.

What is claimed is:

1. A device comprising:

a lithium sulfur redox flow battery comprising an electrolyte composition comprising:

(i) a dissolved Li_2S_x electroactive salt, wherein $x \geq 4$;

(ii) a solvent selected from dimethyl sulfoxide, tetrahydrofuran, or a mixture

thereof; and

(iii) a supporting salt at a concentration of at least 2 M, as measured by moles of supporting salt divided by the volume of the solvent without considering the volume change of the electrolyte after dissolving the supporting salt.

2. The device of claim 1, wherein the electroactive salt is Li_2S_8 .

3. The device of claim 1 or 2, wherein the solvent consists essentially of dimethyl sulfoxide.

4. The device of claim 1 or 2, wherein the solvent consists of dimethyl sulfoxide.

5. The device of any one of claims 1 to 4, wherein the supporting salt is selected from lithium trifluoromethanesulfonate, lithium bis(trifluoromethanesulphonyl) imide, LiCF_2CO_2 , LiNO_3 , or a mixture thereof.

6. The device of claim 5, wherein the supporting salt is selected from lithium trifluoromethanesulfonates or lithium bis(trifluoromethanesulphonyl) imide.

7. The device of any one of claims 1 to 6, further comprising a lithium metal anode.

8. The device of any one of claims 1 to 7, wherein the electrolyte composition is a catholyte.

9. The device of any one of claims 1 to 8, further comprising:

a first half cell part comprising a current collector and the electrolyte composition, wherein the electrolyte composition is a catholyte; and

a second half cell part comprising a lithium metal anode.

10. The device of claim 9, wherein the current collector comprises carbon felt.

11. The device of any one of claims 1 to 10, wherein the supporting salt is lithium bis(trifluoromethanesulphonyl) imide at a concentration of 2M to 4M.

12. The device of claim 11, wherein the solvent consists essentially of dimethyl sulfoxide.

13. An energy storage system comprising:

a lithium sulfur redox flow battery comprising an electrolyte composition comprising:

(i) a dissolved Li_2S_x electroactive salt, wherein $x \geq 4$;

(ii) a solvent selected from dimethyl sulfoxide, tetrahydrofuran, or a mixture

thereof; and

(iii) a supporting salt at a concentration of at least 2 M, as measured by moles of

supporting salt divided by the volume of the solvent without considering the volume change of the electrolyte after dissolving the supporting salt; and

a source of the electrolyte composition fluidly coupled to the lithium sulfur redox flow battery.

14. The system of claim 13, wherein the lithium sulfur redox flow battery comprises:

a first half cell part comprising a current collector and the electrolyte composition, wherein the electrolyte composition is a catholyte; and

a second half cell part comprising a lithium metal anode;

wherein the source of the electrolyte composition is fluidly coupled to the first half cell part.

FIG. 1

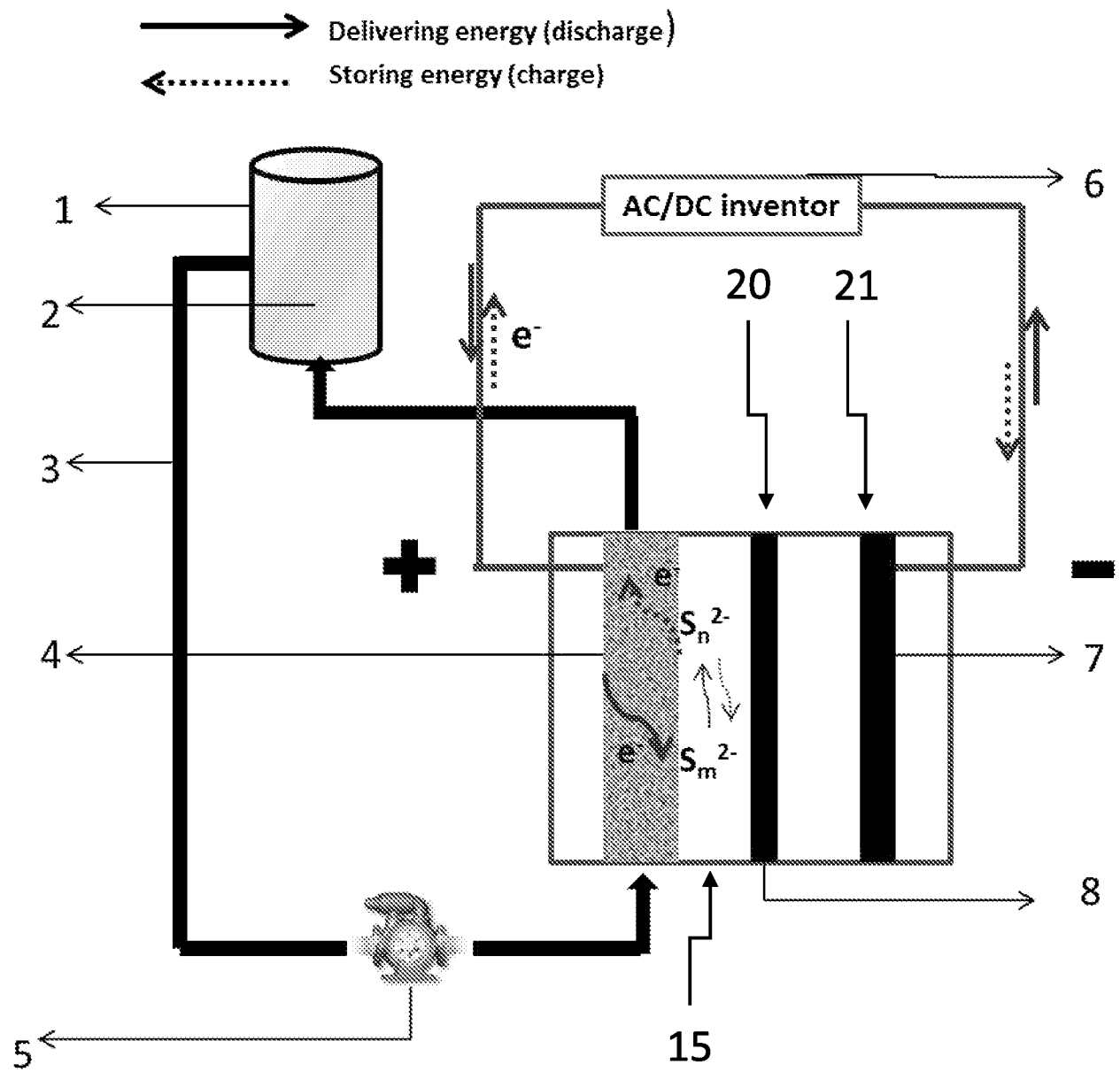


FIG. 2

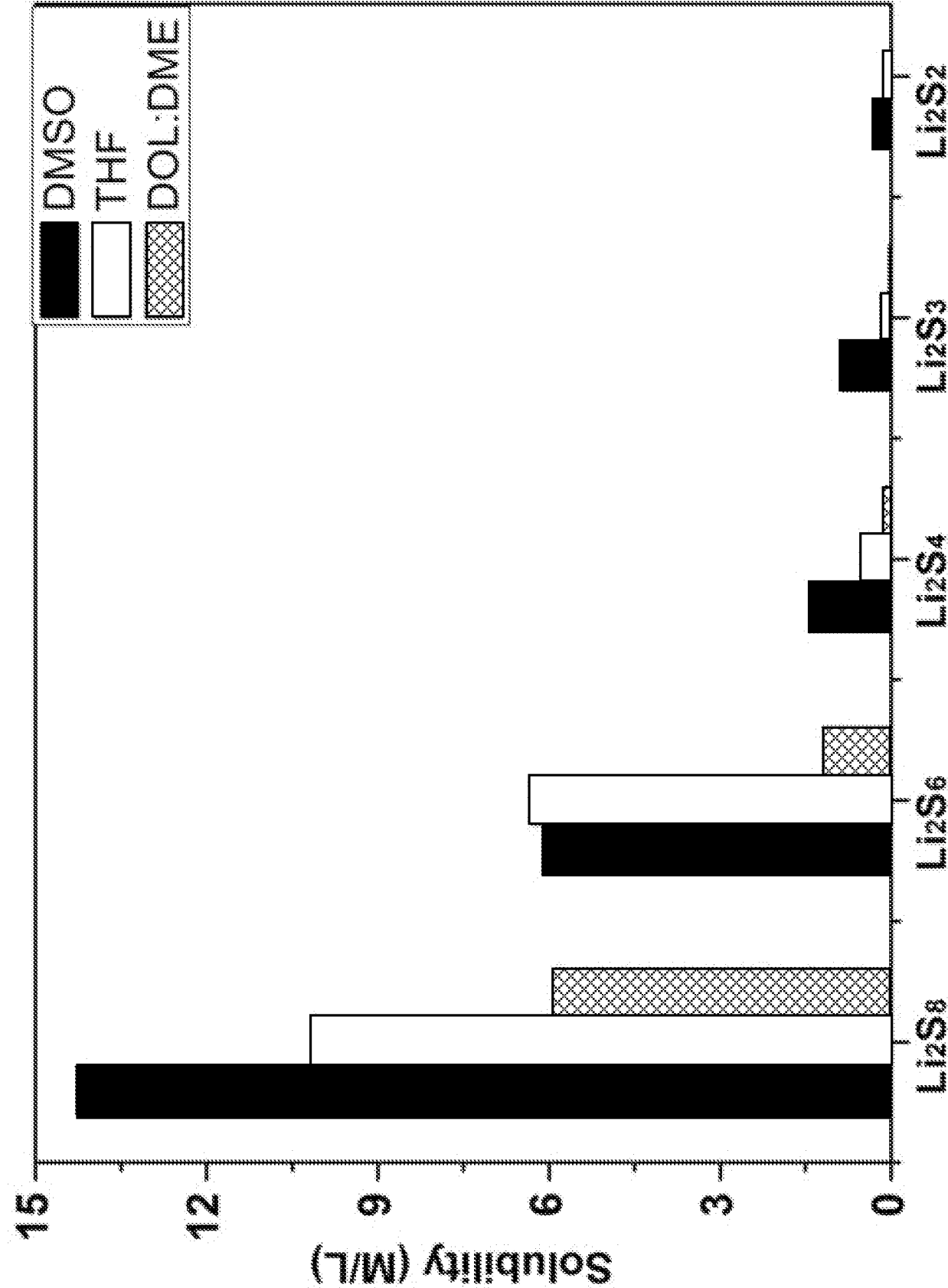


FIG. 3

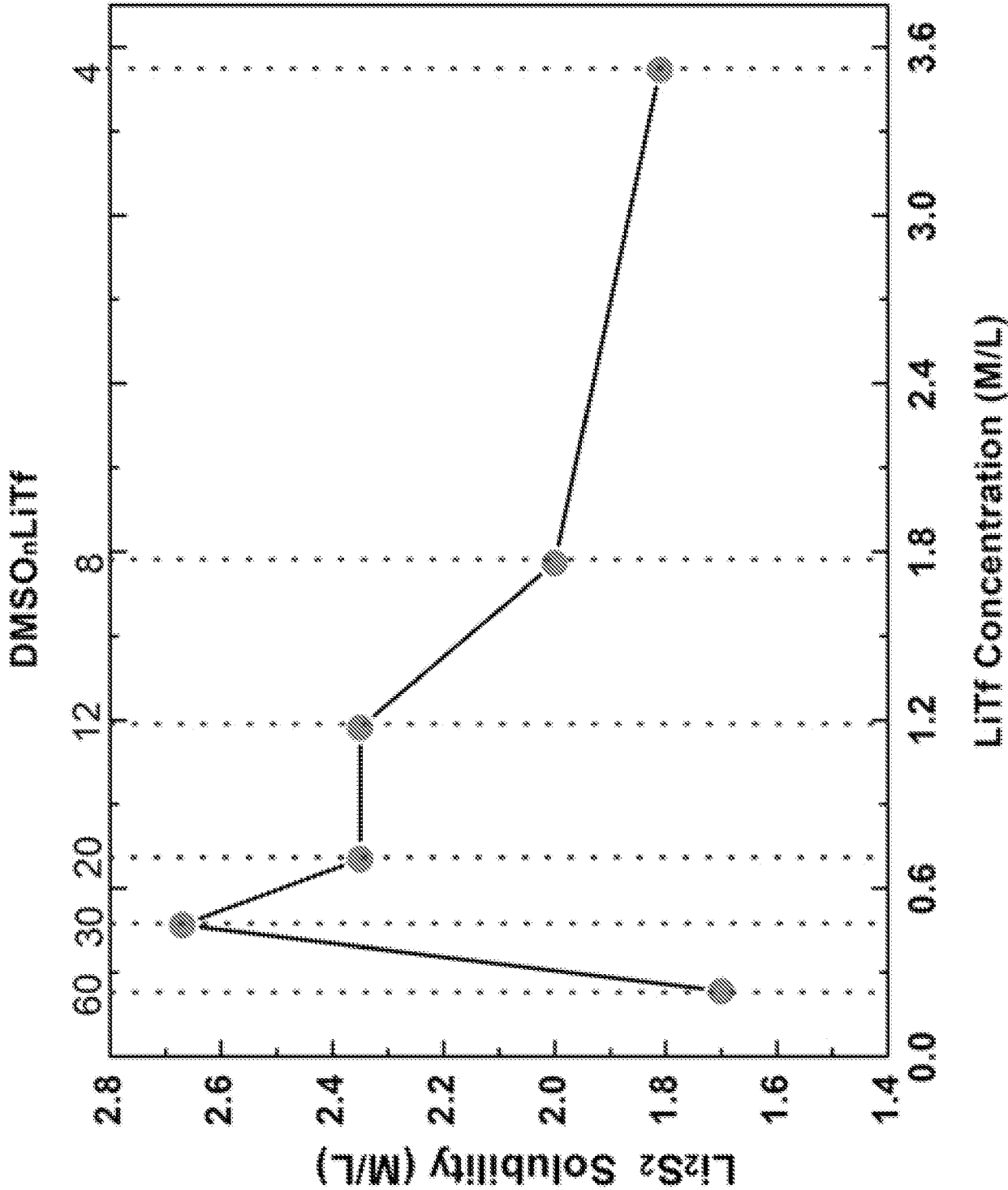


FIG. 4

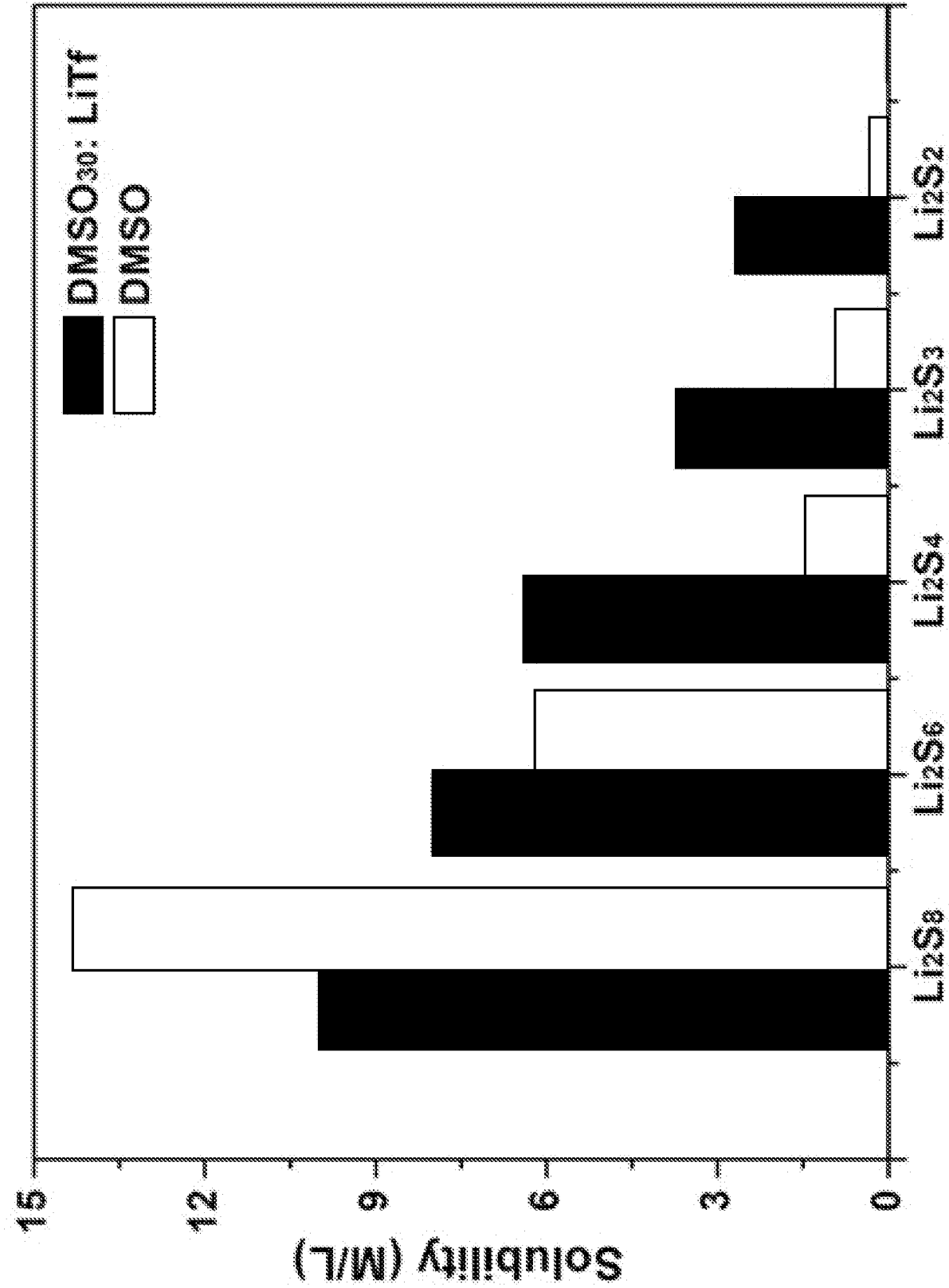


FIG. 5A

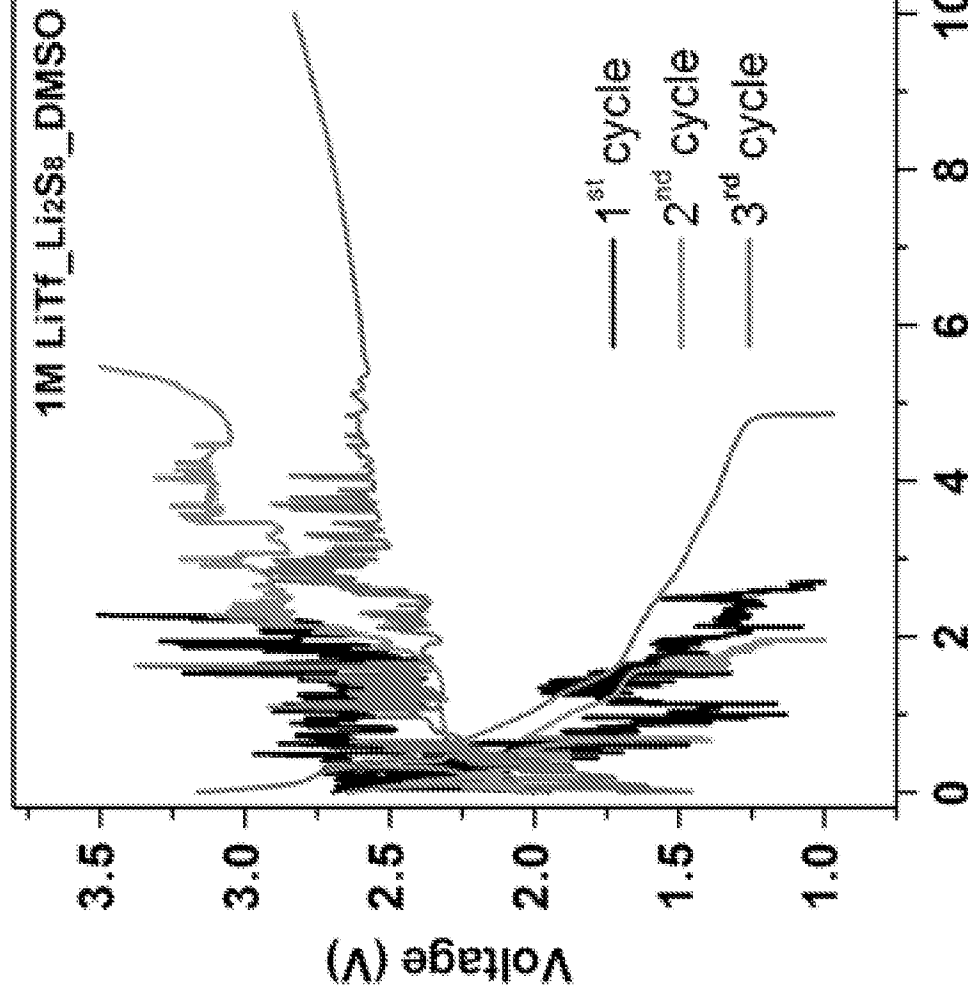
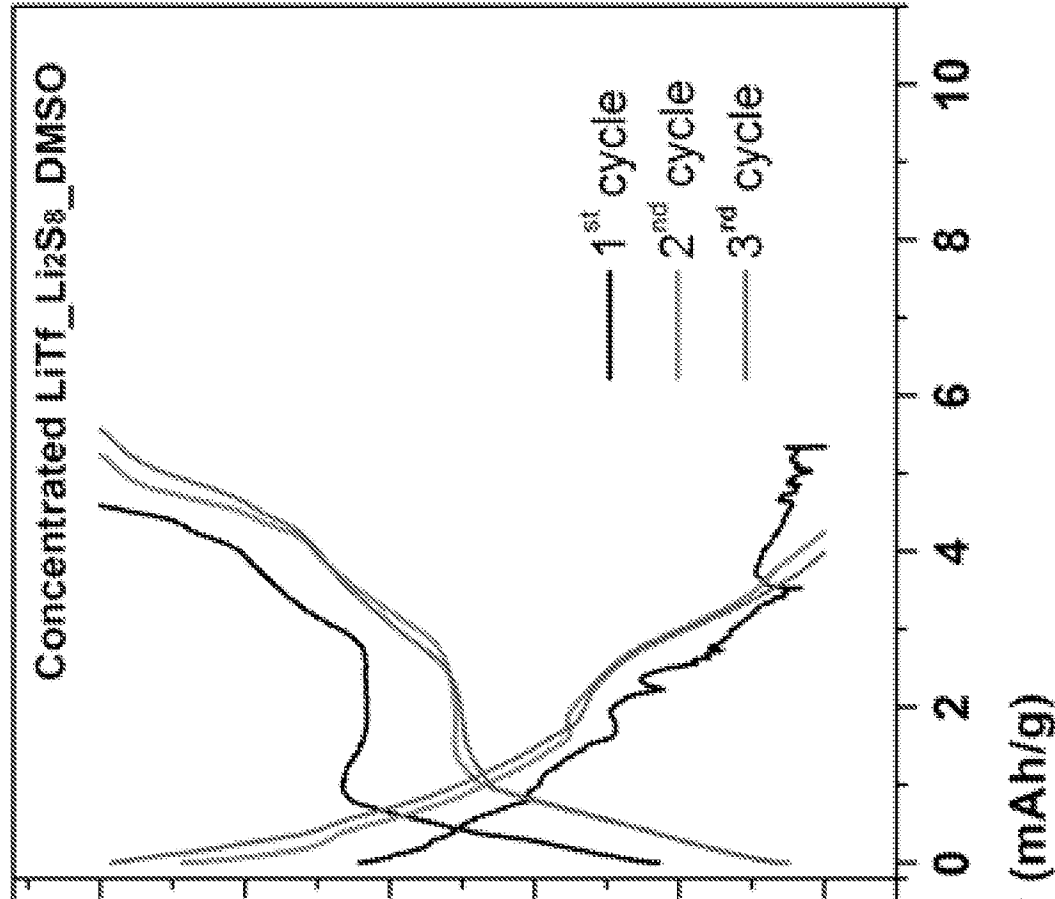


FIG. 5B



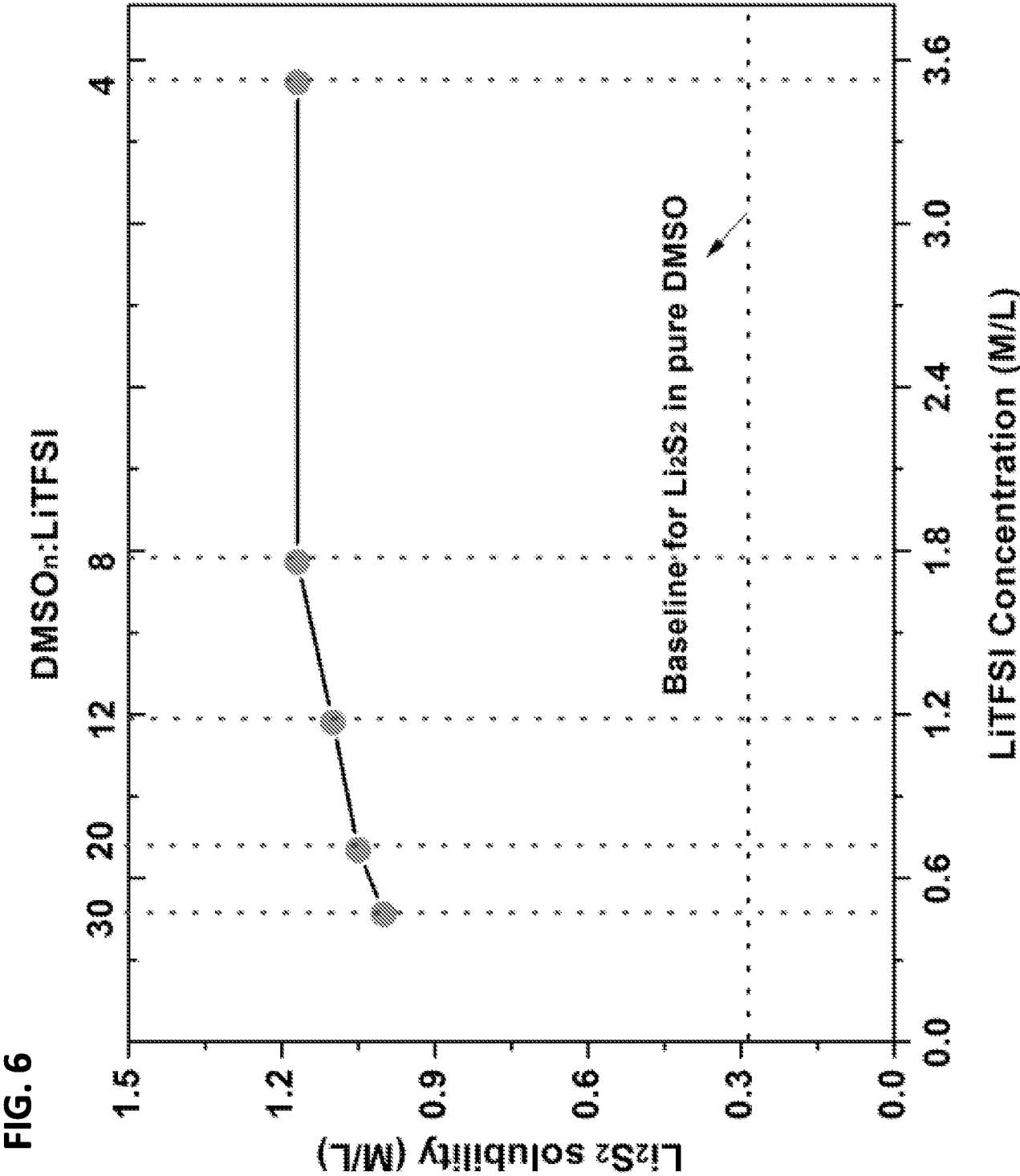


FIG. 7A

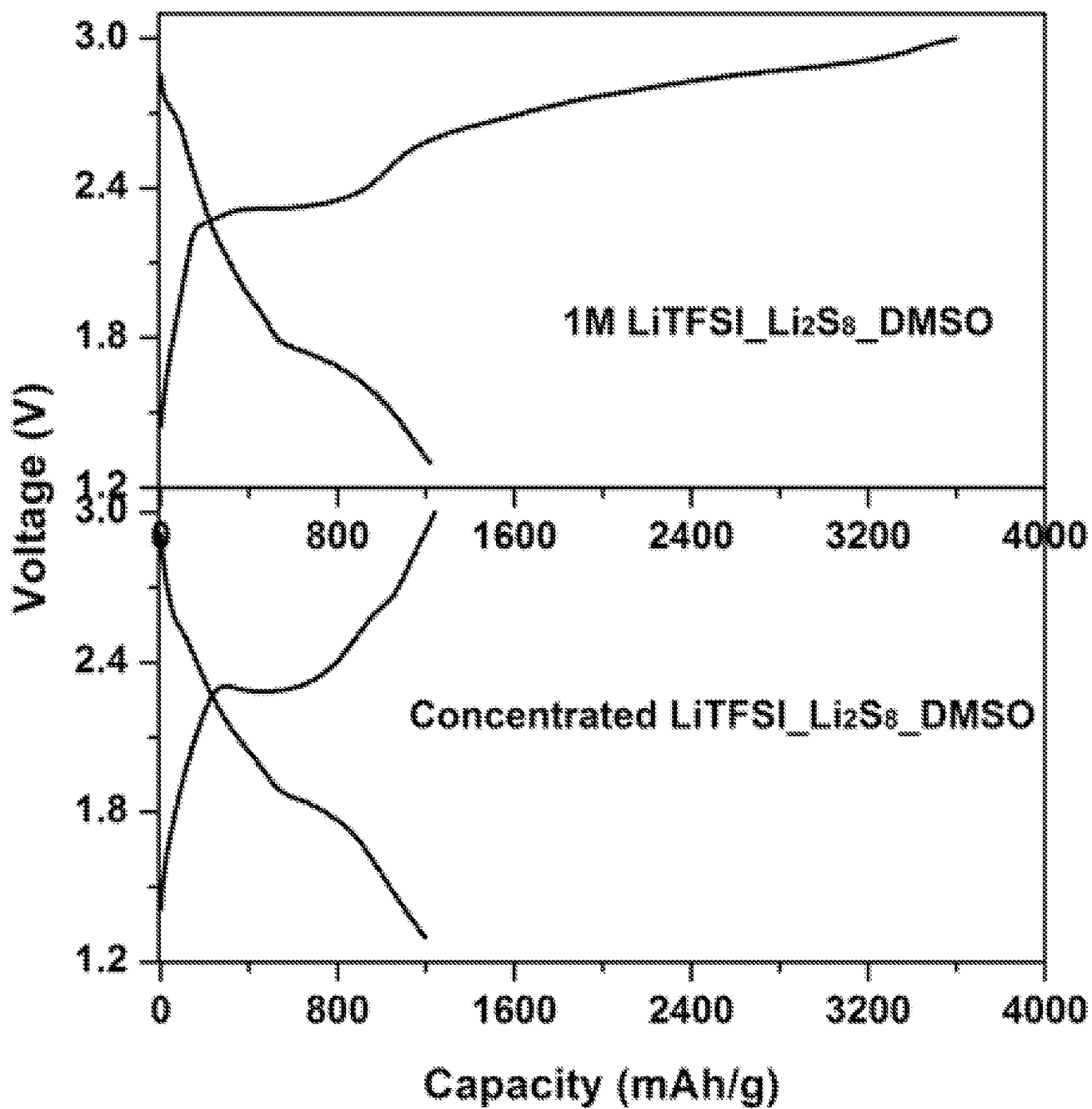
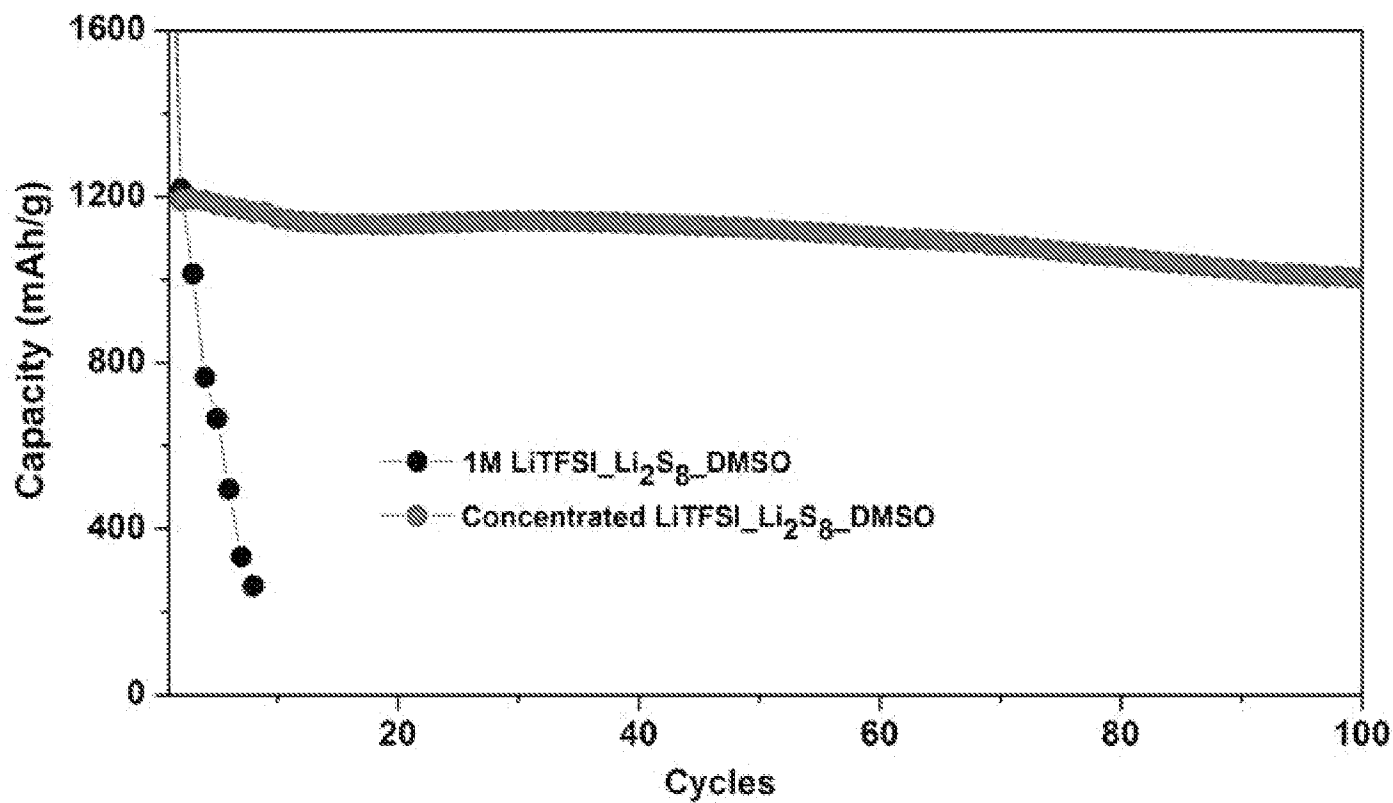
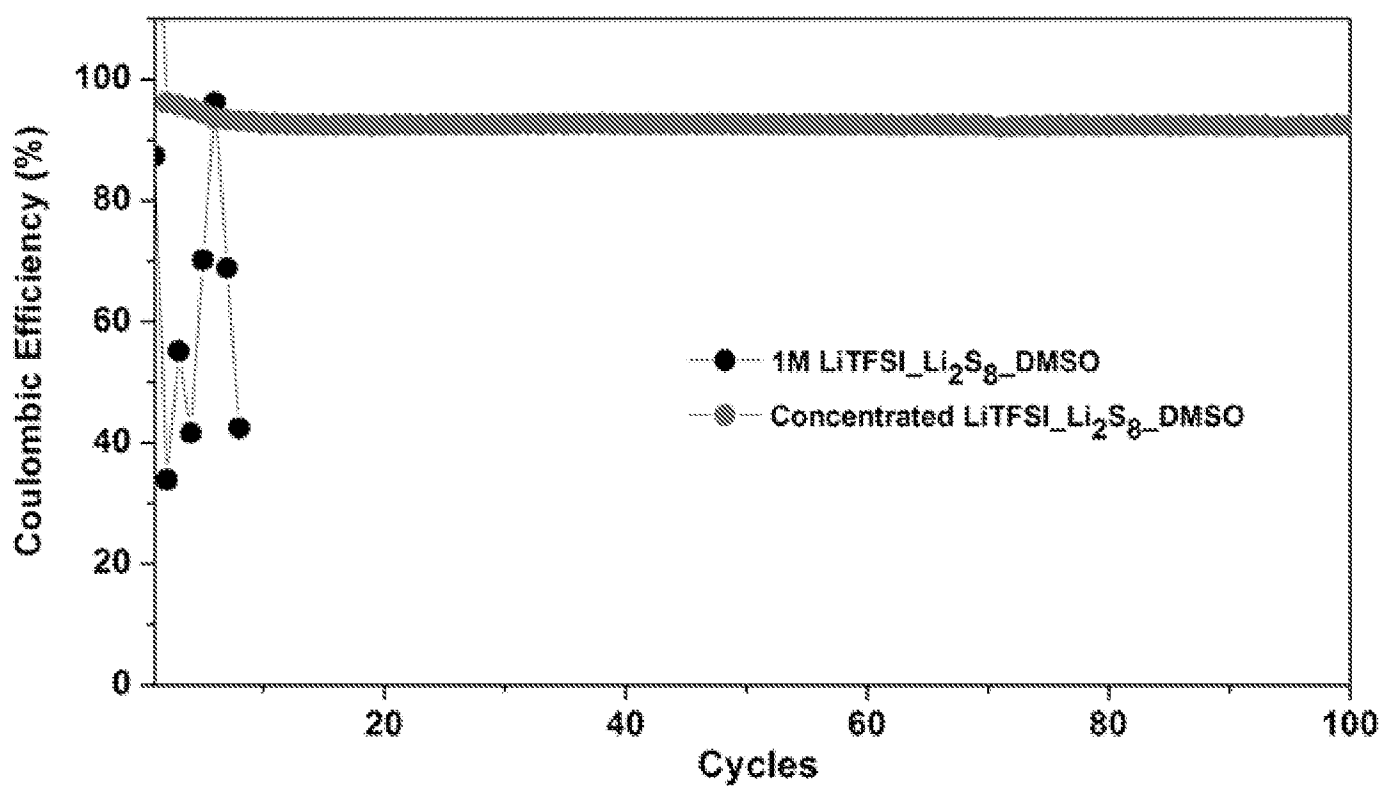


FIG. 7B

FIG. 8A**FIG. 8B**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2015/058131

A. CLASSIFICATION OF SUBJECT MATTER

IPC (2016.01) H01M 8/18, H01M 4/13, C25B 15/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC (2016.01) H01M 8/18, H01M 4/13, C25B 15/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Databases consulted: Esp@cenet, Google Patents, PatBase

Search terms used: (Lithium OR Li) AND (sulf* OR S) AND (dimethyl sulfoxide OR DMSO OR (CH₃)₂SO OR tetrahydrofuran OR THF OR (CH₂)₄O) AND (lithium trifluoromethanesulfonate OR lithium bis(trifluoromethanesulphonyl) imide OR LiCF₂CO₂ OR LiNO₃ OR Lithium nitrate)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2012135278 A1 Tomohisa Yoshie et al 31 May 2012 (2012/05/31) Paragraphs [0016], [0054], [0066]-[0068], [0083]	1-14
A	US 2014302370 A1 Massachusetts Institute of Technology 09 Oct 2014 (2014/10/09) All document	1-14
A	US 2013224538 A1 Uchicago Argonne Llc 29 Aug 2013 (2013/08/29) All document	1-14

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“E” earlier application or patent but published on or after the international filing date

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

20 Jan 2016

Date of mailing of the international search report

20 Jan 2016

Name and mailing address of the ISA:

Israel Patent Office

Technology Park, Bldg.5, Malcha, Jerusalem, 9695101, Israel

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/058131

Patent document cited search report	Publication date	Patent family member(s)	Publication Date
US 2012135278 A1	31 May 2012	US 2012135278 A1	31 May 2012
		CN 102804470 A	28 Nov 2012
		CN 102804470 B	15 Apr 2015
		JP 5417441 B2	12 Feb 2014
		WO 2010143634 A1	16 Dec 2010
US 2014302370 A1	09 Oct 2014	US 2014302370 A1	09 Oct 2014
		WO 2014121276 A2	07 Aug 2014
		WO 2014121276 A3	06 Nov 2014
US 2013224538 A1	29 Aug 2013	US 2013224538 A1	29 Aug 2013
		US 2014370405 A1	18 Dec 2014